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Functionalized p-Phenylene Sulfides Synthesis of New Molecular Wires

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Abstract: Molecular wires containing p-phenylene sulfide units were synthesized. They could be used in material sciences and in supramolecular chemistry. Wires having 2 to 6 phenyl rings were functionalized at one end by an SH or SMe group, and at the other end, by an OH, OMe or OiPr groups. Formation of Ar-S bonds in the chain was achieved by Pd- or Cu-catalyzed couplings of aromatic thiols with aromatic halides. Conditions for a clean chemoselective deprotection of thiols from thiomethyl groups were developed.

Although several methods have been developed to generate poly(p-phenylene sulfide) polymers (PPS),[1] little is known about the synthesis of pure, short PPS oligomers.[2] Only a few of them have been isolated after PPS polymerization, but in rather poor yields (less than 5%).[3] We report here practical syntheses of bifunctionalized poly(p-phenylene sulfide) wires with chain length varying from two to six phenyl rings. These oligomers were functionalized at one end by an SH or SMe group, and at the other end, by an OH, OMe or OiPr functions. The latent nucleophilic hydroxyl functionality was ready to be further functionalized by alkylation. Because of this work, PPS molecular wires could now be used in material sciences; as self-assembled monolayers on gold, as doped conductors or as building blocks in supramolecular chemistry. Finally, thiomethylated oligomers represent soluble models in the study of PPS polymers.

As shown in Table 1, the synthesis of PPS wires required some difficult Ar-S bond formations from the coupling of aromatic thiolates with aromatic halides. Those aromatic substitutions are normally achieved under vigorous heating conditions with unactivated halides in polar aprotic solvents at high temperatures (often above 150°C).[4] For making Ar-S bonds, we chose the Cu_2O-catalyzed method of Adams because of its efficiency and generality.[5] However, the drawback was still the high temperature needed (about 160°C) and some disulfide formation.[6] As a milder complementary method, $Pd(PPh_3)_4$ was used as a catalyst with aromatic bromides and thiolates at 100-110°C.[7,8] Although short p-phenylene sulfides from two to four phenyl units are efficiently made, the yields of Ar-S couplings drop as the chain length increases to five or six phenyl units. On one occasion, deoxygenation of the mixture by bubbling N_2 before heating increased the yield from 29 to 63% (Entry no 8, Table 1).

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PII: S0040-4039(97)10624-4

Table 1: Synthesis of Polyphenylene Sulfide Wires[a]

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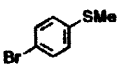
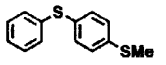
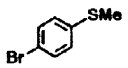
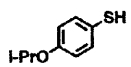
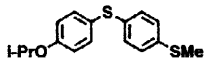
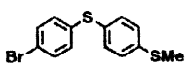
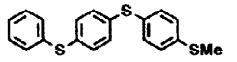
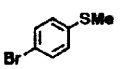
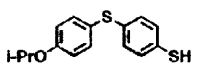
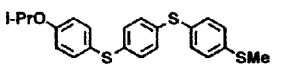
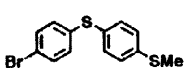
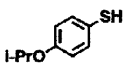
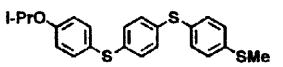
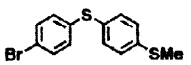
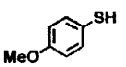
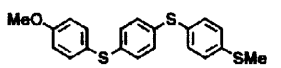
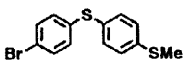
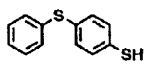
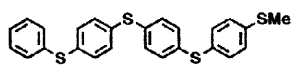
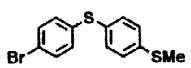
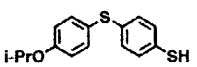
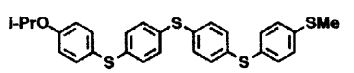
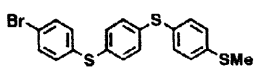
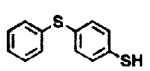
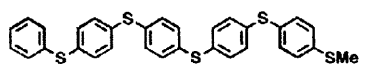
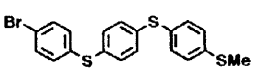
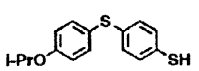
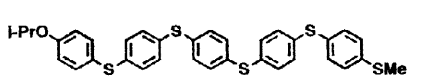
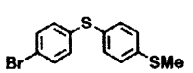
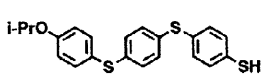
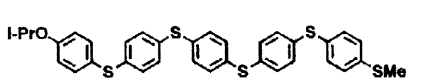
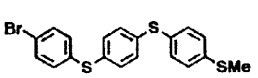
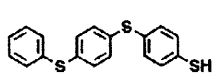
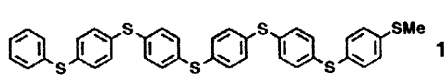
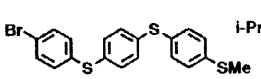
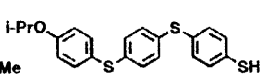
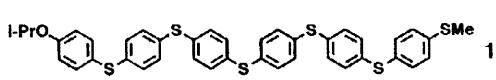
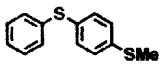
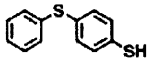
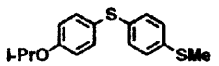
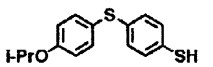
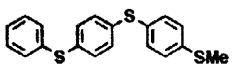
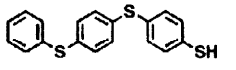
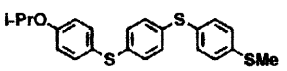
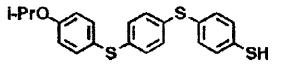
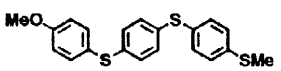
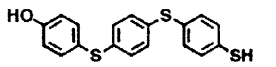
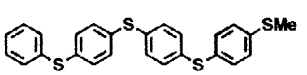
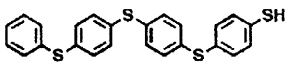
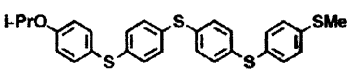
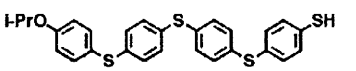
1			A		99%
2			B		90%
3			A		70%
4			A B		53% 60%
5			B		52%
6			A		40%
7			A		70%
8			A C B		29% 63% 40%
9			A		21%
10			B		33%
11			B		21%
12			A		11%
13			B		12%

a: Wires were characterized by ^{1}H, ^{13}C and MS HRes (EI)

b: METHOD A: Cu_2O, Pyridine/Quinoline (1:4), 160°C
METHOD B: $Pd(PPh_3)_4$ 5%, NaH, n-BuOH, 100-110°C
METHOD C: Cu_2O, Pyridine/Quinoline (1:4), 160°C
Bubbling of N_2 for 30 min. before heating

Table 2. Synthesis of Thiol Wires[a]

ENTRY NO	ARYL METHYL SULFIDE	CONDITIONS[b]	AROM. THIOL	YIELD
1		A		93%
2		A		80%
3		A		67%
4		A C		75% 76%
5		A B		70% 48%
6		C		92%
7		C		99%

a: Thiols were characterized by ^{1}H, ^{13}C and MS HRes (EI)

b: METHOD A: i-PrSNa (5.0 eq.), DMF, 160°C, 2-3 hrs
METHOD B: MeSNa (5.0 eq.), NMP, 200°C
METHOD C: t-BuSNa (5.0 eq.), DMF, 160°C, 2-3 hrs

In the presence of thiophilic transition metals for making Ar-S bonds, a few protective groups resisted to decomposition under nucleophilic conditions at high temperatures (100-160°C). The chemoselective deprotection of a thiol function in the presence of a protected phenol group guided us toward stable thiomethyl and isopropyloxy groups. As shown in Table 2, general methods for the selective dealkylation of thiomethyl groups were developed because classic reducing conditions with $Na/NH_{3(l)}$ [9] or Na/pyridine[9] at 100°C lead to uncontrolled cleavage of C-S bonds in the chains. Deprotections reported by Tiecco et al. with MeSNa in DMF at 160°C[10] (or NMP at 200°C) most often gave an unseparable mixture of thiol and unreacted material. We developed new conditions with i-PrSNa or t-BuSNa in DMF at 150-160°C. A clean conversion to the thiol group was consistently produced in yields ranging from 70 to 99% within 2-3 hours.

Molecular wires shown in Tables 1 and 2 were fully characterized by ^{1}H, ^{13}C NMR and high resolution MS (EI, 70 eV). All of the aromatic bromides in Table 1 were synthesized in good yields by selective bromination of the appropriate precursors at 100°C in AcOH.[11] Optimization and development of milder methodologies for making Ar-S bond are in progress.

In summary, the syntheses of new bifunctionalized PPS molecular wires of various length have been achieved. Conditions for a clean chemoselective deprotection of thiols from thiomethyl groups were developed. These wires could be used in material sciences and supramolecular chemistry.

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